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(54) **RECORDING MATERIAL FOR INKJET PRINTING**

AUFZEICHNUNGSMATERIAL FÜR DAS TINTENSTRAHL-DRUCKVERFAHREN

MATERIAU D'ENREGISTREMENT POUR IMPRESSION PAR JET D'ENCRE

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EP 0 912 348 B1

Description

[0001] The invention relates to a recording material for inkjet printing, which has the character of paper and whose printed images applied to the recording layer have extremely high water resistance and lightfastness.

Prior Art

[0002] DE 30 18 342 A describes a synthetic paper for inkjet printing which, after printing in the inkjet printer, is rendered transparent by the action of heat in order to obtain multicolor inkjet recordings having high recording density, good color reproduction and high water resistance. The print which initially appears pale acquires high contrast and water resistance only as a result of subsequent melting. Papers of this type then have the disadvantage of low opacity (high transparency). The inventors are attempting to overcome this disadvantage by means of two- or three-ply papers having an opaque layer which cannot be rendered transparent and an outer layer or outer layers which can be rendered transparent and which comprises or comprise plastics fibers. However, fiber-containing recording layers always give an inadequate printed image with respect to defined spot diameter and bleeding of the ink in the recording surface.

[0003] EP-A-01 64 196 discloses a recording layer for inkjet methods on a sheet-like base material which also contains papers of synthetic fibers, the layer containing both a cationic polymer and a polyvalent metal salt for fixing aqueous inks. In addition, water-penetratable or water-swellable binders, such as, for example, polyvinyl alcohol, and pigments, such as, for example, calcium carbonate, kaolin or urea/formaldehyde fillers, may be contained in such a layer. The water resistance of recordings applied by inkjet methods is relatively low owing to the choice of the components used (PVA; polyvalent metal salt; cation polymer) even if the water resistance test described (one minute immersion in water following by drying) is presented as positive. The object of this application was primarily to produce a rapidly drying, stackable (non-offsetting) paper having a brilliant appearance of the recordings.

[0004] DE 4446551 C1 describes a water-resistant recording material comprising a synthetic paper and a pigment layer which is bound to make it water-resistant and which serves for ink absorption. The fixing of the anionic ink dyes is achieved by means of cationic fixing agents so that a recording which is water-resistant overall is achieved. The disadvantage of these layers is the porous structure of the coating, which is capable of further absorption of dyes or foreign substances/impurities, and the low lightfastness and document resistance of the recordings owing to the large internal surface area for the absorption of the ink dyes.

[0005] EP 0575 644 B1 describes a microporous coating by formation of an open-pore polymer matrix on exceeding the solubility limits of the chosen polymer in the solvent (mixture) or by sintering together individual polymer particles. This coating is also said to be printable by inkjet printing, it being possible for the coating to be rendered transparent by means of heat, pressure or solvents after printing, and the absorbed ink dyes thereby being encapsulated. An advantage is the increased durability of the recordings which is present after the imparting of transparency, in particular a durable resolution. The production of such layers is extremely difficult since precipitation reactions of polymers and sintering together of polymers are difficult to control.

[0006] US-A-5,242,739 describes a transfer material for fabrics which comprises a paper, for example a latex-impregnated paper, an optional release layer and a coating of thermoplastic polymer particles and a film-forming binder. The material is first written on or painted by hand or printed by means of mechanical printers (dot matrix printers). The coating with the printed image can then be transferred to textiles at high temperature, for example by ironing, i.e. is not firmly bonded to the substrate material. Suitability for inkjet prints is not mentioned.

[0007] US-A-5,194,317 describes a recording material for inkjet printing, comprising a transparent plastics film as a substrate material and a recording layer which is applied thereon and contains a binder and plastics beads. The publication contains no information on the fusibility of the recording layer.

[0008] For applications outdoors or in the security area under persistent influence of water, humidity and light, inkjet papers known to date are unsuitable without further process steps, such as, for example, overlamination with film, since the water resistance of the base papers and of the printed recording layer is insufficient. Precisely in applications such as, for example, construction plans, maps, layout plans, labels, signs, markings, passes, tickets and securities, inkjet prints which are mechanically stable and have unlimited color stability even under the influence of water, humidity and light are required.

[0009] It is therefore the object of the present invention to provide a recording material for inkjets printing which is suitable for the application described and resists any type of humidity or water influence and the influence of light. Both mechanical strength of the substrate paper under the influence of water and water resistance and light stability of the inkjet image are required for this purpose. Furthermore, a brilliant, high-contrast, colored or black inkjet print with high resolution and very crisp edges is required.

Summary of the Invention

[0010] According to the invention, this object is achieved by a recording material for the inkjet method with aqueous inks, comprising a substrate paper which contains synthetic fibers and has a content of from 10% by weight to 90% by weight of cellulose fibers and a content of from 40% by weight to 1% by weight of synthetic fibers and a binder content of from 50% by weight to 5% by weight, based on the total weight of the substrate paper, and comprising a fiber-free porous recording layer which is arranged on one or both main surfaces of the substrate paper and consists of from at least 60% by weight to 95% by weight of finely divided unfused thermoplastic particles having a mean particle size of from 0.5 to 40 µm, a self-supporting film according to ISO R527, produced from said unfused thermoplastic particles by fusion, having an elongation at break of more than 5% and a tensile strength of more than 5 MPa, and, as the remainder, of film-forming binders and, if required, inorganic pigments and assistants and additives conventional in such layers; and wherein after action of heat on the recording layer and formation of a cohesive film of fused or sintered plastics particles, and after storage for 1 week in water at 30°C, the recording material still has 80% of the tear strength of the dry paper, measured according to DIN 53128, based on the initial value after the heat treatment.

[0011] The mean particle size of the plastics particles is preferably from 5 µm to 20 µm.

[0012] The achievement of the object includes a process for the production of a stable recording on a recording material as claimed in one or more of patent claims 1-9 by producing one-color or multicolor recordings by applying ink(s) by means of inkjet methods and subsequently treating the printed recording layer with heat at temperatures of 80-200°C, preferably 100-180°C, in order to form a cohesive film from the fused or sintered plastics particles, and the optical density, measured according to DIN 4512 of colored recordings of the primary colors applied by said inkjet method is after storage for 1 week in water at 30°C still at least 90%, based on the initial values after the heat treatment.

[0013] Preferably, the surface of the recording layer is subjected to high pressure in addition to the heat.

Detailed description of the invention

[0014] The substrate paper preferably also contains fillers and/or pigments in addition to the cellulose fibers and the binder or binders, the binder content being correspondingly reduced by their presence. Suitable pigments are kaolin, barium sulfate, calcium carbonate, calcium sulfate and TiO_2. The pigment/filler content may be from 2.0% by weight to 30% by weight. The wet strength of the substrate paper may be adjusted by the concomitant use of crosslinking agents for the binder and/or wet strength agents, depending on the requirements. Preferred binders are polyvinyl acetate, polyvinyl acetate copolymers, styrene/butadiene copolymers, styrene/butadiene/acrylonitrile terpolymers, styrene/(meth)acrylate copolymers (meth)acrylic polymers, ethylene/(meth)acrylic acid copolymers, polyvinyl alcohol, carboxymethylcellulose, hydroxyethylcellulose, starch, starch derivatives, casein or mixtures thereof. Such film-forming polymers are commercially available.

[0015] For example, melamine/formaldehyde resins or urea/formaldehyde resins may be used as crosslinking agents. The substrate paper is produced on conventional paper machines by known methods and is provided with the binder preferably in the size press and/or by subsequent coating in a conventional coating machine. For example, polyamide fibers, polyester fibers, viscose fibers, polyethylene fibers or mixtures thereof may be present as synthetic fibers in the substrate paper. The basis weight of the substrate paper may be from 50 g/m^2 to 300 g/m^2, preferably from 80 g/m^2 to 200 g/m^2.

[0016] By subsequently applying the binder to the entire surface, it is also possible to ensure that the coated or impregnated substrate paper does not absorb water or absorbs water only very slowly. It is particularly advantageous if such a coating is applied before the application of the porous, fiber-free recording layer capable of forming the film. This coating or impregnation of the substrate paper prevents ink dyes applied to the porous recording layer during printing from penetrating into the substrate paper and hence not being fixed in the recording layer during the subsequent heat treatment and any pressure treatment.

[0017] Owing to the low absorptivity of the substrate paper for aqueous inks, direct printing by means of an inkjet printer gives a poorly drying non-water-resistant image which has run. The substrate paper itself has excellent wet strength, which is manifested by high tear strength in the completely wet state.

[0018] A porous recording layer which can rapidly absorb the ink applied in the inkjet method and gives high-resolution images/prints having crisp edges is therefore applied to one side or both sides of this substrate paper. This coating contains from 60% to 95% of finely divided hydrophobic thermoplastic particles having a mean particle size between 1 µm and 40 µm, preferably from 5 to 20 µm. Furthermore, this coating contains one or more film-forming binders and further conventional assistants, such as, for example, wetting agents, antifoams, inorganic pigments, fillers, dyes, UV absorbers, plasticizers and antioxidants. The initially porous recording layer is formed from an aqueous or solvent-containing coating composition by application to the substrate paper and drying at temperatures, in the recording layer, below the softening temperature of the thermoplastic particles. However, the plastics particles can be fused or sintered by the action of heat and, if required, pressure on the recording layer to give a cohesive film. The porous structure of

the recording layer is substantially destroyed and a film of the thermoplastic particles (organic pigment particles) forms, in which the further components of the layer and the applied ink dyes are enclosed and thus fixed.

[0019] Surprisingly, it was found that. after printing and heat/pressure treatment, the combination of the special paper, which contains synthetic fibers, with recording layers based on thermoplastic organic pigments leads to an abrasion-resistant and extremely water-resistant recording material which retains its strength even, for example, after storage for 1 week in water, and the applied image information is abrasion-resistant and shows virtually no loss of contrast under the action of water. Furthermore, the recordings thus obtained have extremely high light stability, in contrast to the inkjet prints known to date and the printed material not converted into a film.

[0020] The porous recording layer formed on the synthetic base paper permits rapid ink absorption and fixing of the dyes contained in the printing ink. Furthermore, the recording layer must adhere well to the base paper, both in the wet and in the dry state, before and in particular after said layer has been converted into a film. The recording layer itself must have sufficiently high cohesion per se so that moderate mechanical stress due to flexing, pleating, folding or rubbing, for example during the printing process, does not lead to damage to the layer or to the printed image. After film formation, the recording layer must not be damaged even under high stresses.

[0021] To ensure good absorptivity of aqueous inks, a hydrophobic thermoplastic pigment which has a mean particle size of between 0.5 µm and 40 µm, preferably from 5 to 20 µm, is preferably used in the recording layer. The individual polymer particles may be spherical or in the form of hollow spheres; the pigment preferably consists of irregularly shaped particles. The melting point of the polymer used for the particles should be between 80°C and 200°C, preferably between 100°C and 160°C. If it is lower, coating of the polymer particles from a suspension/emulsion is not possible without premature melting and binding together of the particles during formation of the layer; if the melting point is higher, the treatment step to be carried out after printing is often not possible without decomposition of the coating or of the substrate material. The particle size distribution of the pigments may be broad or narrow; sufficient ink absorptivity of the coating owing to its porosity is important for the choice. In particular, porous thermoplastic pigments having a high cavity volume, as can be obtained in the precipitation of polymers from solution, are advantageous for this purpose.

[0022] Water-insoluble homopolymers or copolymers of the following classes of compounds may be used as polymers for the thermoplastic pigment: polyacrylates, polymethacrylates, polyesters, polyamides, polyurethanes, polyethylene, polypropylene, polystyrene, polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, cellulose derivatives, starch derivatives and polyepoxides. The presence of defined particles having a predetermined size and shape is important for the choice of a suitable thermoplastic pigment, in order to obtain coatings which are as porous as possible for rapid ink absorption. It is advantageous to use particles as can be obtained, for example, during mechanical comminution, for example milling, of polymers or during precipitation of polymers from solution. The dried coating should therefore have a porosity of at least 0.2 ml/g, which is to be determined by the gravimetric absorption of water in the course of 1 minute on dried coating material. The mean particle size of the thermoplastic pigments should be between 0.5 and 40 µm, preferably between 5 µm and 20 µm, in order to ensure optimum drying during printing, crisp edges and high resolution. Layers having smaller pigment particles dry more poorly while layers having a mean particle size of more than 40 µm are rough and do not give images having crisp edges.

[0023] Mechanical properties of the thermoplastic pigments essentially determine the properties of the layer in the form of a film. A self-supporting film produced from the unfused thermoplastic pigment particles by fusiuon has an elongation at break of more than 5%, in particular more than 20%, and a tensile strength of more than 5 MPa (ISO R 527). A mechanically stable, flexible recording layer is thus obtained on the base paper after film formation.

[0024] In order to obtain a recording layer which is abrasion-resistant prior to film formation, it is necessary to choose, for the thermoplastic pigment, a binder which, after drying of the generally aqueous coating composition, fixes the pigment particles on the substrate paper without reducing the porosity of the layer too greatly. Plastics dispersions, such as, for example, vinyl acetate homopolymers or copolymers, acrylate (co)polymers, styrene/butadiene copolymers, ethylene or vinyl chloride copolymers and polyurethane dispersions have proven particularly suitable for this purpose. In order to ensure flexibility of the layer and adhesion to the paper, dispersions having a minimum film formation temperature between -20°C and +50°C, preferably between -10°C and +20°C, are preferably used.

[0025] Water-soluble binders, such as, for example, polyvinyl alcohol, polyvinylpyrrolidone, starch, starch derivatives, polyacrylamide, casein, water-soluble or ammonia-soluble polyacrylates or polymethacrylates and copolymers thereof, for example with styrene, cellulose derivatives, such as cellulose ether and carboxymethylcellulose, may furthermore be used. In order to increase the strength further, it is possible to incorporate into the coating solution crosslinking agents which react when the layer is dried. Suitable substances include urea/formaldehyde or melamine/formaldehyde resins, aziridines, polyfunctional isocyanates and boric acid (for PVA).

[0026] Furthermore, optical brighteners, wetting agents, further pigments in small amounts, for example silica, aluminum hydroxides or aluminas, kaolin or calcium carbonate, and dyes for colored papers, adhesion promoters, antifoams, thickeners (for example acrylate dispersions, polyacrylic acid, etc.), dispersants, etc. may be present as assistants in the layer. In order to influence the melting point, the softening temperature and the flow behavior of the thermoplastic pigment, a plasticizer may also be used. Suitable plasticizers are available for virtually all polymers, for

example phthalates and fatty esters.

[0027] The use of assistants for fixing the anionic ink dyes is possible but not preferred. The cationic polymers usually used for fixing the anionic dyes, such as, for example, cationic acrylates, acrylamides, polydiallyldimethylamine chloride, polyallylamine, polydiallylamine, polyimine, etc., generally have an adverse effect on the lightfastness. The use of such compounds must therefore be checked for their effects with regard to lightfastness of the ink dyes.

[0028] The ink absorption layer is applied to the synthetic paper by applying the coating composition with the aid of conventional coating methods, for example by roller application and metering with an air brush or rotating doctor, preferably from aqueous dispersion, and is dried with hot air. The amount of the dried coating composition applied is between 10 and 50 g/m^2, preferably from 25 to 40 g/m^2. This applied amount is necessary for rapid adsorption of the ink liquid in the coating during printing and hence for preventing running of the image lines. The weight of recording layer applied can be varied depending on the printer and amount of ink to be subsequently used.

[0029] The ink absorption layer of the present invention adheres sufficiently to the synthetic base paper and, prior to film formation, has good cohesion and flexibility so that it withstands mechanical stresses. After film formation, the load capacity increases so that it is extremely difficult to damage mechanically, both in the dry and in the wet state. This is necessary, for example, in all applications in which forgery-proof characteristics, document security, etc. must be ensured.

[0030] After printing by means of inkjet printing, the paper is brought to a temperature above the melting point/softening point of the thermoplastic pigment used, the pore structure of the coating being destroyed and a thermoplastic film which contains the assistants used and the applied ink dyes being formed. This aftertreatment of the print results in the ink dyes becoming insensitive to the influence of water. This applies both to the water-soluble, generally anionic dyes used in conventional aqueous inkjet inks and to pigment colorants. Surprisingly, it was also found that the light stability of the heat-treated prints increases to an extreme extent, in particular when soluble dyes are used. The formation of a plastics film from the layer containing the thermoplastic pigment can be accelerated and completed by the additional influence of pressure.

[0031] Suitable methods for film formation are available, for example IR irradiation, hot pressing, ironing, heatable rollers or fixing means, are to be found in copiers or hot lamination apparatuses.

[0032] As a result of the film formation, the surface becomes water-repellent and therefore cannot absorb further ink. This helps to make the prints very forgery-proof. Furthermore, it is as a rule unnecessary to apply a protective laminating film over the print. This has enormous advantages with regard to the process and costs.

[0033] The coated paper also has high resistance to mechanical stress, i.e. initial tearing and complete tearing of the paper is possible only with a great deal of force, both in the dry and in the wet state. In the completely wet state, the paper has in particular over 80% of the tear strength of the dry paper, measured according to DIN 53128.

[0034] The paper described in the present invention can be printed on commercial inkjet printers with a high-contrast, high-resolution image which has crisp edges and is colored in the case of color printers. The paper rapidly absorbs the generally aqueous or predominantly aqueous ink in the coating and is dry and smudge-resistant shortly after printing. Suitable printers are, for example, printers which operate with aqueous inks according to the bubble jet principle, the piezoelectric principle or the continuous inkjet method, as offered in various versions, for example by Canon, Epson, Hewlett Packard, Iris, Lexmark, Encad, etc. Both small-size (DIN A3 and A4) and large-size prints, for example on rolls for posters, are possible. In addition to water and anionic dyes, the inks used in the abovementioned printers contain, as a rule, further assistants, such as, for example, high-boilers (glycols, NMP, etc.) and wetting agents.

[0035] After the heat treatment, the printed image is extremely resistant to flexing, pleating, folding and scratching, both in the wet and in the dry state, so that the image information is completely retained even under extreme environmental conditions. Inks which have high light stability to UV light too are preferably chosen for image production. Owing to the fixing of the dyes and the water resistance of the coating itself, the material withstands even the prolonged action of water. Thus, the color intensity (contrast) of the printed image does not decrease or decreases only slightly in the course of storage for 1 week in water at 30°C. In any case, the color stability under these conditions is so good that, after this treatment, the optical density of colored surfaces of the primary colors black, cyan, magenta, yellow, blue, red and green is still at least 90%, based on the initial values.

[0036] As a result of the film formation, the light stability of ink dyes increases. Particularly in the case of water-soluble dyes, an increase in the lightfastness by a factor of 2 or more is found, which increase can be calculated from the quotient of the exposure times to UV light up to the time when a printed colored surface has only 90% of the optical density of the fresh print.

[0037] The papers described in this application are suitable for intended uses in which very high stresses occur, in particular in association with humidity or water or the influence of light. Thus, for example, construction plans, maps, layout plans, posters, labels, banners, flags, signs, markings, passes, tickets and securities can be produced from the papers and, after printing and film formation, have very high mechanical strength under all conditions and an indestructible printed image substantially stable to environmental influences. Particularly in the case of securities, security features may additionally be incorporated or applied, such as, for example, fluorescent prints or fibers, magnetic stripes,

laminating films, RF circuits, etc.

Test methods:

Tear strength of the wet paper and stability of the printed image

[0038] A test image which contains in particular relatively large color surfaces of all primary colors (cyan, magenta, yellow and black) and of the binary mixed colors (blue, green and red) is applied to the inkjet paper according to the invention by means of an inkjet printer. 10 minutes after production of the test image, the recording layer is converted into a film by means of a hot press. After cooling, the recording sheet is completely immersed in water at 30°C for 1 week. After this storage time, the mechanical strength of the paper is determined in the longitudinal direction and transverse direction in the wet state according to DIN 53128 (tear strength). The tear strength of the dry paper conditioned at 23°C and 50% relative humidity is also determined.

[0039] Furthermore, the paper stored in water for 1 week is dried in a drying oven at 80°C for 5 minutes. Subsequently, as directly after conversion of the test prints into a film, the optical density of each colored surface is determined by means of an RD 920 densitometer from MacBeth according to DIN 4512. The percentage residual value of the optical density, calculated from the measurements before and after storage of the respective colored area in water, is a measure of the change in the printed surfaces or of the fixing of the dyes of the inkjet inks. The colors black, red, green and blue were measured densitometrically without filters, and the colors yellow, magenta and cyan with the appropriate filters.

[0040] The light stability is determined by means of a UV accelerated weathering apparatus (Suntest from Haereus). For this purpose, the surfaces of the four primary colors black, cyan, magenta and yellow described above are exposed and are measured regularly using the abovementioned densitometer with color filters. The plot of the measured values as a function of time then permits the evaluation of the color stability under UV light, for example by extension of the time until the measured values decrease to 90% of the initial measured values.

Example 1

[0041] A commercial synthetic paper (Pretex KL 43.095 from Papierfabrik Lahnstein GmbH, Lahnstein) of 95 g/m² and comprising 18% of cellulose fibers, 33% of synthetic fibers, 18% of binders, 28% of pigments and assistants is coated with the following coating material in a coating weight (solid) of 40 g/m² by means of a rotating doctor and is dried in a drying oven at 100°C for 5 minutes:

Water	40.0 g
Rhopaque HP91, styrene/acrylate hollow bodied dispersion (from Rohm & Haas) mean particle size 1.05 µm; 25% strength	85.0 g
Polyvinyl alcohol (MOWIOL 4/88, from Hoechst)	2.0 g
Ammonia (25% strength)	1.5 g
Polyethylene glycol, molar mass 400 g/mol	2.0 g
Wetting agent (SURFYNOL 440, Air Products Inc.)	0.5 g

[0042] The coating material has a solids content of about 19% by weight and a pH of 7.5. It contains 84%, based on the solid substance, of thermoplastic pigment.

[0043] The matt paper coated in this manner is printed with a test print by means of a Novajet III inkjet printer from Encad using commercial ink cartridges from American Inkjet Corp. and the coating is converted into a film at 140°C by means of a hot press in the course of 30 seconds. After this treatment, the now glossy print shows a high-contrast, high-resolution image having crisp edges. It has extremely high water resistance: the image-bearing paper stored for 1 week in water at 30°C has a tear strength (Elmendorf, DIN 53128) of 3.8 N in the longitudinal direction and of 4.0 N in the transverse direction, compared with 2.1 N in the longitudinal direction and 2.7 N in the transverse direction in the dry state.

[0044] As a result of the water treatment, the colored surfaces exhibit only very little or no color changes compared with the initial color values (Table 1).

[0045] The lightfastness of the printed parts is increased by at least a factor of 2 (cf. Table 2) compared with the material not converted into a film. After film formation, scarcely any change in a print is detectable even after UV irradiation for 200 hours.

Example 2

[0046] A commercial synthetic paper (Pretex KL 30.120 from Papierfabrik Lahnstein GmbH, Lahnstein) of 120 g/m², comprising 61% of cellulose fibers, 4% of synthetic fibers, 12% of synthetic binders and assistants and precoated on both sides with about 5 g/m² of a plastics dispersion comprising styrene/butadiene copolymer is coated with the following coating material in a coating weight (solid) of 35 g/m² by means of a rotating doctor and is dried in a drying oven at 100°C for 5 minutes:

Water	156.0 g
Precipitated copolyamide having a melting point of 140°C (mixture of ORGASOL 3501 ExDNAT1 and ORGASOL 3502 DNAT1, ELF ATOCHEM S.A.), bimodal average particle size 10 μm and 20 μm	68.0 g
Plastics dispersion (50% solids) of vinyl acetate copolymer (Vinnapas EP 400, Wacker Chemie GmbH, Munich) having a minimum film formation temperature of 0°C and a mean particle size 0.8 μm	18.4 g
Thickener: polyacrylate (STEROCOLL D, BASF AG)	4.0 g
Ammonia: (25% strength)	3.5 g
Plasticizer: N-n-butylbenzenesulfonamide	7.0 g
Wetting agent (SURFYNOL 440, Air Products Inc.)	1.5 g

[0047] The coating material has a solids content of about 33% by weight and a pH of 8.5. It contains 78%, based on the solid substance, of thermoplastic pigment.

[0048] The matt paper coated in this manner is printed with a test print by means of a Novajet III inkjet printer from Encad using commercial ink cartridges from American Inkjet Corp. and the coating is converted into a film at 160°C by means of a hot press in the course of one minute. After this treatment, the now glossy print shows a high-contrast, high-resolution image having crisp edges. It has extremely high water resistance. The image-bearing paper stored for one week in water at 30°C has a tear strength (Elmendorf, DIN 53128) of 4.0 N in the longitudinal direction and 4.2 N in the transverse direction, compared with 2.4 N in the longitudinal direction and 2.8 N in the transverse direction in the dry state.

[0049] As a result of the water treatment, the color surfaces show only very little or no color changes compared with the initial color values (Table 1). The UV stability of the colored surfaces is excellent. The printed image exhibits virtually no change even after more than 200 hours (Table 2).

Example 3

[0050] A commercial synthetic paper (Pretex KL 43.095, Papierfabrik Lahnstein GmbH, Lahnstein) of 95 g/m² and comprising 18% of cellulose fibers, 33% of synthetic fibers, 18% of binders, 28% of pigments and assistants is coated with the following coating material in a coating weight (solid) of 40 g/m² by means of a rotating doctor and is dried in a drying oven at 100°C for 5 minutes:

Water	155.0 g
Precipitated copolyamide having a melting point of 140°C (mixture of ORGASOL 3501 ExDNAT1 and ORGASOL 3502 DNAT1, ELF ATOCHEM S.A.), bimodal average particle size 10 μm and 20 μm	77.9 g
Styrene/butadiene copolymer dispersion (50% solid) (LITEX PS 5520, Hüls AG)	26.3 g
Thickener (ROHAGIT S hv, Rohm GmbH)	0.4 g
Ammonia (25% strength)	8.4 g
Plasticizer: N-n-butylbenzenesulfonamide	5.8 g
Wetting agent (SURFYNOL 440, Air Products Inc.)	0.34 g
Dispersant (CARBOSET 524 H, BF Goodrich) 40% strength dispersion	5.7 g

[0051] The coating composition has a solids content of about 36% by weight and a pH of 10. It contains 76%, based on the total solid in the composition, of thermoplastic pigment.

[0052] The matt paper coated in this manner is printed with a test image by means of a NOVAJET III inkjet printer from Encad using commercial ink cartridges from American Inkjet Corp. and the coating is converted into a film at 160°C by means of a hot press in the course of one minute. After this heat treatment, a high-contrast image having crisp edges is present. The recording has very high water resistance. The material provided with an inkjet print and stored for one week in water at 30°C has a tear strength (Elmendorf, DIN 53128) of 3.9 N in the longitudinal direction and 4.0 N in the transverse direction, compared with 2.4 N in the longitudinal direction and 2.8 N in the transverse

direction in the dry state.

[0053] As a result of the water treatment, the colored surfaces show only very little or no color changes compared with the initial color values (Table 1). The UV stability of the colored surfaces is excellent. The printed image shows virtually no change even after over 200 hours (Table 2).

Comparative Example

[0054] The paper from Example 1 is coated and printed as described there. However, the test for resistance to water and UV light is carried out in the state without converting to a film (without heat treatment). The water resistance of the prints (Table 3) is insufficient since the ink dyes are dissolved to a great extent from the porous, printed layers. Furthermore, the coating of the synthetic paper in the wet state can be readily damaged mechanically so that the printed image is destroyed. The light stability is poor; under UV irradiation, the colors fade very rapidly (Table 2).

Table 1:

Percentage residual value of the optical density after storage for 1 week in water at 30°C, in %							
Example	**Black**	**Cyan**	**Magenta**	**Yellow**	**Blue**	**Red**	**Green**
1	96	98	93	99	100	98	97
2	92	94	99	94	93	96	98
3	94	94	98	96	95	96	97
Comparison	20	36	41	67	45	56	41

Table 2

Light stability of the primary colors				
Example 1				
Time in SUNTEST	Optical density (Macbeth densitometer RD 920)			
	Black	Cyan	Magenta	Yellow
0 hours	1.53	1.36	1.21	1.06
72 hours	1.54	1.33	1.18	1.06
144 hours	1.52	1.30	1.12	1.05
216 hours	1.48	1.29	1.10	1.03
Example 2				
Time in SUNTEST	Optical density (Macbeth densitometer RD 920)			
	Black	Cyan	Magenta.	Yellow
0 hours	1.57	1.54	1.53	1.43
72 hours	1.53	1.54	1.51	1.42
144 hours	4.45	1.48	1.42	1.41
216 hours	1.43	1.43	1.31	1.41
Example 3				
Time in SUNTEST	Optical density (Macbeth densitometer RD 920)			
	Black	Cyan	Magenta	Yellow
0 hours	1.55	1.49	1.48	1.39
72 hours	1.54	1.49	1.46	1.38
144 hours	1.42	1.45	1.40	1.37
216 hours	1.41	1.41	1.35	1.36

Table 2 (continued)

Light stability of the primary colors				
Comparative Example				
Time in SUNTEST	Optical density (Macbeth densitometer RD 920)			
	Black	Cyan	Magenta	Yellow
0 hours	1.53	1.36	1.21	1.06
72 hours	1.28	1.26	0.65	0.87
144 hours	1.15	1.21	0.37	0.74
216 hours	1.04	1.19	0.27	0.6

Claims

1. A recording material for the inkjet method with aqueous inks, comprising a substrate paper which contains synthetic fibers and has a content of from 10% by weight to 90% by weight of cellulose fibers and a content of from 40% by weight to 1% by weight of synthetic fibers and a binder content of from 50% by weight to 5% by weight, based on the total weight of the substrate paper, and comprising a fiber-free porous recording layer which is arranged on one or both main surfaces of the substrate paper and consists of from at least 60% by weight to 95% by weight of finely divided unfused thermoplastic particles having a mean particle size of from 0.5 to 40 µm, a self-supporting film according to ISO R527. produced from said unfused thermoplastic particles by fusion, having an elongation at break of more than 5% and a tensile strength of more than 5 MPa, and, as the remainder, of film-forming binders and, if required, inorganic pigments and assistants and additives conventional in such layers; and wherein after action of heat on the recording layer and formation of a cohesive film of fused or sintered plastics particles, and after storage for 1 week in water at 30°C, the recording material still has 80% of the tear strength of the dry paper, measured according to DIN 53128, based on the initial value after the heat treatment.

2. The recording material as claimed in claim 1, wherein the substrate paper contains polyamide fibers, polyester fibers, polyethylene fibers, viscose fibers or mixtures thereof as synthetic fibers.

3. The recording material as claimed in claim 1, wherein the recording media contains 1-30% by weight of film-forming binders selected from polyvinyl acetate, polyvinyl acetate copolymers, styrene/butadiene copolymers, styrene/butadiene/acrylonitrile terpolymers, styrene/(meth)acrylate copolymers, (meth)acrylic polymers, ethylene/(meth)acrylic acid copolymers, ethylene or vinyl chloride copolymers, polyvinyl alcohol, polyvinylpyrrolidone, cellulose derivatives or mixtures thereof.

4. The recording material as claimed in claim 1, wherein the thermoplastic particles have a mean particle size of from 5 µm to 20 µm.

5. The recording material as claimed in claim 1, wherein the finely divided thermoplastic particles are selected from polyolefins, polyester, polyamide, polyurethane, polyimide, poly(meth)acrylate or polyepoxide.

6. The recording material as claimed in claim 5, wherein the thermoplastic particles are porous.

7. The recording material as claimed in claim 5 or 6, wherein the thermoplastic particles are composed of a polyamide (co)polymer.

8. The recording material as claimed in claim 7, wherein the thermoplastic particles are composed of polyamide 6, polyamide 12 or copolyamide 6/12.

9. The recording material as claimed in any of claims 1-8, wherein the porous recording layer can be fused or sintered at temperatures of 80-200°C to give a cohesive film.

10. A process for the production of a stable recording on a recording material as claimed in one or more of patent claims 1-9 by producing one-color or multicolor recordings by applying ink(s) by means of inkjet methods and

subsequently treating the printed recording layer with heat at temperatures of 80-200°C, preferably 100-180°C, in order to form a cohesive film from the fused or sintered plastics particles, and the optical density, measured according to DIN 4512 of colored recordings of the primary colors applied by said inkjet method is after storage for 1 week in water at 30°C still at least 90%, based on the initial values after the heat treatment.

11. The process as claimed in claim 10, wherein, in addition to the heat, the surface of the recording layer is subjected to high pressure.

Patentansprüche

1. Aufzeichnungsmaterial für das Tintenspritzverfahren mit wäßrigen Tinten, enthaltend ein Trägerpapier, das synthetische Fasern enthält und einen Gehalt von 10 Gew.-% bis 90 Gew.-% Cellulosefasern und einen Gehalt von 40 Gew.-% bis 1 Gew.-% synthetische Fasern und einen Bindemittelgehalt von 50 Gew.-% bis 5 Gew.-%, bezogen auf Gesamtgewicht des Trägerpapiers, aufweist, und eine faserfreie poröse Aufzeichnungsschicht, die auf einer oder beiden Hauptoberflächen des Trägerpapiers angeordnet ist und aus mindestens 60 Gew.-% bis 95 Gew.-% feinteiligen nichtverschmolzenen thermoplastischen Teilchen mit einer mittleren Teilchengröße von 0,5 bis 40 µm und als den verbleibenden Rest aus filmbildenden Bindemitteln und, falls erforderlich, anorganischen Pigmenten und in solchen Schichten üblichen Hilfsmitteln und Zusätzen besteht, wobei ein nach ISO R527 aus den nichtverschmolzenen thermoplastischen Teilchen durch Verschmelzen hergestellter selbsttragender Film eine Bruchdehnung von mehr als 5% und eine Reißfestigkeit von mehr als 5 MPa aufweist, und wobei nach Einwirkung von Wärme auf die Aufzeichnungsschicht und Ausbildung eines zusammenhängenden Films von verschmolzenen oder versinterten Kunststoffteilchen und nach einwöchiger Lagerung in Wasser bei 30°C das Aufzeichnungsmaterial noch 80% der Reißfestigkeit des trockenen Papiers, bezogen auf den Anfangswert nach Wärmebehandlung, gemessen nach DIN 53128, aufweist.

2. Aufzeichnungsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß das Trägerpapier Polyamidfasern, Polyesterfasern, Polyethylenfasern, Viskosefasern oder Mischungen derselben als synthetische Fasern enthält.

3. Aufzeichnungsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß das Aufzeichnungsmaterial 1 bis 30 Gew.-% filmbildende Bindemittel enthält, ausgewählt aus Polyvinylacetat, Polyvinylacetatcopolymeren, Styrol/Butadien-Copolymeren, Styrol/Butadien/Acrylnitril-Terpolymeren, Styrol/(Meth)acrylat-Copolymeren, (Meth)acrylpolymeren, Ethylen/(Meth)acrylsäure-Copolymeren, Ethylen- oder Vinylchlorid-Copolymeren, Polyvinylalkohol, Polyvinylpyrrolidon, Cellulosederivaten oder Mischungen derselben.

4. Aufzeichnungsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß die thermoplastischen Teilchen eine mittlere Teilchengröße von 5 bis 20 µm aufweisen.

5. Aufzeichnungsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß die feinteiligen thermoplastischen Teilchen aus Polyolefinen, Polyester, Polyamid, Polyurethan, Polyimid, Poly(meth)acrylat oder Polyepoxid ausgewählt sind.

6. Aufzeichnungsmaterial nach Anspruch 5, dadurch gekennzeichnet, daß die thermoplastischen Teilchen porös sind.

7. Aufzeichnungsmaterial nach Anspruch 5 oder 6, dadurch gekennzeichnet, daß die thermoplastischen Teilchen aus einem Polyamid-(Co)polymer sind.

8. Aufzeichnungsmaterial nach Anspruch 7, dadurch gekennzeichnet, daß die thermoplastischen Teilchen aus Polyamid 6, Polyamid 12 oder Copolyamid 6/12 sind.

9. Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß die poröse Aufzeichnungsschicht bei Temperaturen von 80 bis 200°C zu einem zusammenhängenden Film verschmolzen oder versintert werden kann.

10. Verfahren zur Herstellung einer stabilen Aufzeichnung auf einem Aufzeichnungsmaterial nach einem oder mehreren der Patentansprüche 1 bis 9 durch Herstellen einfarbiger oder mehrfarbiger Aufzeichnungen durch Aufbringen von Tinte(n) mittels Tintenspritzverfahren und anschließendes Behandeln der bedruckten Aufzeichnungsschicht mit Wärme bei Temperaturen von 80 bis 200°C, vorzugsweise 100 bis 180°C, um einen zusammenhängenden Film aus verschmolzenen oder versintertem Kunststoffteilchen auszubilden, und wobei die optische Dich-

te, gemessen nach DIN 4512, von farbigen Aufzeichnungen der durch Tintenspritzverfahren aufgebrachten Grundfarben nach einwöchiger Lagerung in Wasser bei 30°C noch mindestens 90%, bezogen auf die Anfangswerte nach Wärmebehandlung, beträgt.

11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß zusätzlich zu Wärme die Oberfläche der Aufzeichnungsschicht hohem Druck ausgesetzt wird.

Revendications

1. Matériau d'enregistrement pour impression par jet d'encre avec des encres aqueuses, comprenant un papier formant substrat qui contient des fibres synthétiques et a une teneur en fibres de cellulose comprise entre 10 % en poids et 90 % en poids, une teneur en fibres synthétiques comprise entre 40 % en poids et 1 % en poids et une teneur en liant comprise entre 50 % en poids et 5 % en poids, sur la base du poids total du papier formant substrat, et comprenant une couche d'enregistrement poreuse dépourvue de fibres qui est disposée sur une ou sur les deux surfaces principales du papier formant substrat et se compose d'au moins 60 % en poids à 95 % en poids de particules thermoplastiques non fondues finement divisées ayant une granulométrie moyenne comprise entre 0,5 et 40 µm, un film auto-porteur selon la norme ISO R527, produit par fusion à partir desdites particules thermoplastiques non fondues, ayant un allongement à la rupture supérieur à 5 % et une résistance à la traction supérieure à 5 MPa, et, pour le reste, des liants filmogènes et, si nécessaire, des pigments minéraux et des adjuvants et additifs classiques dans ces couches ; et dans lequel, après action de la chaleur sur la couche d'enregistrement et formation d'un film cohésif de particules plastiques fondues ou frittées, et après stockage pendant une semaine dans de l'eau à 30°C, le matériau d'enregistrement présente encore 80 % de la résistance au déchirement du papier sec, mesurée selon la norme DIN 53128, en se basant sur la valeur initiale après traitement thermique.

2. Matériau d'enregistrement selon la revendication 1, dans lequel le papier formant substrat contient des fibres de polyamide, des fibres de polyester, des fibres de polyéthylène, des fibres de viscose ou des mélanges de celles-ci en tant que fibres synthétiques.

3. Matériau d'enregistrement selon la revendication 1, dans lequel le support d'enregistrement contient de 1 à 30 % en poids de liants filmogènes choisis parmi l'acétate de polyvinyle, les copolymères d'acétate de polyvinyle, les copolymères de styrène/butadiène, les terpolymères de styrène/butadiène/acrylonitrile, les copolymères de styrène/méthacrylate, les polymères méthacryliques, les copolymères d'éthylène/acide méthacrylique, les copolymères d'éthylène ou de chlorure de vinyle, l'alcool polyvinylique, la polyvinylpyrrolidone, les dérivés de la cellulose ou des mélanges de ceux-ci.

4. Matériau d'enregistrement selon la revendication 1, dans lequel les particules thermoplastiques ont une granulométrie moyenne comprise entre 5 µm et 20 µm.

5. Matériau d'enregistrement selon la revendication 1, dans lequel les particules thermoplastiques finement divisées sont choisies parmi les polyoléfines, le polyester, le polyamide, le polyuréthane, le polyimide, le polyméthacrylate ou le polyépoxyde.

6. Matériau d'enregistrement selon la revendication 5, dans lequel les particules thermoplastiques sont poreuses.

7. Matériau d'enregistrement selon l'une des revendications 5 ou 6, dans lequel les particules thermoplastiques se composent de (co)polymère d'un polyamide.

8. Matériau d'enregistrement selon la revendication 7, dans lequel les particules thermoplastiques se composent de polyamide 6, polyamide 12 ou de copolyamide 6/12.

9. Matériau d'enregistrement selon l'une quelconque des revendications 1 à 8, dans lequel la couche d'enregistrement poreuse peut être fondue ou frittée à des températures comprises entre 80°C et 200°C pour donner un film cohésif.

10. Procédé pour produire un enregistrement stable sur un matériau d'enregistrement selon une ou plusieurs des revendications 1 à 9, en produisant des enregistrements monochromes ou polychromes en appliquant une (ou des) encre(s) au moyen d'impressions par jet d'encre et ensuite en traitant la couche d'enregistrement imprimée par la chaleur à des températures comprises entre 80 et 200°C, de préférence comprises entre 100 et 180°C, afin

de former un film cohésif à partir des particules plastiques fondues ou frittées, la densité optique, mesurée selon la norme DIN 4512 d'enregistrements en couleur des couleurs primaires appliquées par ladite impression par jet d'encre étant, après un stockage d'une semaine dans de l'eau à 30°C, encore d'au moins 90 %, en se basant sur les valeurs initiales après traitement thermique.

11. Procédé selon la revendication 10, dans lequel, en plus de la chaleur, la surface de la couche d'enregistrement est soumise à une pression élevée.